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硕 士 学 位 论 文

低温水热一步法制备  $\text{Ag/TiO}_2$ 、 $\text{W/TiO}_2$  和  
 $(\text{Ag}, \text{W})/\text{TiO}_2$  及其表征

Preparation of  $\text{Ag/TiO}_2$ ,  $\text{W/TiO}_2$  and  $(\text{Ag}, \text{W})/\text{TiO}_2$  by a  
One-Step Low-Temperature Hydrothermal Method and  
their Characterizations

王 笛

指导教师姓名: 周 忠 华 教 授

专 业 名 称: 材 料 学

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## 摘要

近十年,  $\text{TiO}_2$  光催化材料因其安全性、稳定性、高效性和低成本, 在降解环境污染物领域受到广泛关注。但锐钛矿  $\text{TiO}_2$  仍存在光子利用率低、光生电子空穴对复合迅速等缺点有待改善。

锐钛矿  $\text{TiO}_2$  表面负载贵金属, 能形成 Schottky 势垒; 作为电子捕获剂有效阻止光生电子空穴对的复合。过渡金属掺杂可改变  $\text{TiO}_2$  的晶体结构和禁带宽度, 影响光谱响应范围。本文以提高  $\text{TiO}_2$  光催化活性, 制备同时对液相和气相有良好适应性的光催化剂为目的, 以钛酸正丁酯和金属盐为原料, 在水溶液中, 用低温水热一步法, 制备了结晶态纳米 Ag 负载、W 掺杂和 Ag/W 双元素负载/掺杂的锐钛矿  $\text{TiO}_2$  纳米颗粒。通过扫描电镜、透射电镜、X 射线衍射、X 光电子能谱、紫外-可见漫反射光谱和荧光光谱对其结构和形貌进行了表征, 并通过光催化降解  $\text{H}_2\text{S}$  气体和亚甲基蓝溶液, 评价了光催化性能。分析了产物结构、形貌、负载/掺杂量与性能之间的关系, 提出了低温水热一步法的反应机理。

实验结果显示, (1) 低温水热一步法制备的 Ag 负载  $\text{TiO}_2$ , 与传统的光还原沉积法不同, Ag 为结晶态 (通常光还原法得到的为非晶态), 因此, 更容易捕获  $\text{TiO}_2$  光生电子, 抑制了  $\text{TiO}_2$  光生电子和空穴复合, 提高了对  $\text{H}_2\text{S}$  的光催化降解性能; Ag/ $\text{TiO}_2$  对  $\text{H}_2\text{S}$  的吸附性能与 Ag 单质含量成正比; 光催化降解性能 Ag=4.5 wt% 时效果最好, 为  $\text{TiO}_2$  的 3.1 倍; (2) 制备的 W 掺杂  $\text{TiO}_2$ ,  $\text{W}^{6+}$  进入晶格替代  $\text{Ti}^{4+}$ , 形成  $\text{W}_x\text{Ti}_{1-x}\text{O}_2$  固溶体, 有利于  $\text{TiO}_2$  的热稳定性; 对  $\text{TiO}_2$  光催化降解亚甲基蓝有促进作用, W=3 wt% 时光催化降解效果最好; (3) 制备的 Ag/W 负载/掺杂  $\text{TiO}_2$ ,  $\text{W}^{6+}$  进入晶格, 结晶态纳米 Ag 负载在表面, 禁带宽度为 3.0 eV, 扩大了  $\text{TiO}_2$  的光响应范围; 光催化降解亚甲基蓝能力介于 W/ $\text{TiO}_2$  与 Ag/ $\text{TiO}_2$  之间, Ag/W 最佳比例为 1:2; 光催化降解  $\text{H}_2\text{S}$  能力高于  $\text{TiO}_2$ ; (Ag, W)/ $\text{TiO}_2$  在同时具备良好的液相和气相光催化降解性能方面具有潜力。

低温水热一步法具备许多优点。工艺设备、条件简单, 低成本; 一步即可制备出产物, 且负载贵金属为晶态, 不需二次加热; 无需其他添加剂, 只在水溶液中进行。金属离子和 Ti 的前驱体均匀混合, 具有高结晶度和良好分散性; 通过

调节前驱体含量、水热温度，可控制产物中纳米金属的晶粒、结晶度。是一种极具潜力的贵金属负载  $\text{TiO}_2$  纳米颗粒制备方法。

关键词： $\text{TiO}_2$ ；低温水热一步法；结晶 Ag 负载；W 掺杂；光催化

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## Abstract

In recent decades,  $\text{TiO}_2$  photocatalytic materials have been of more and more interests in degradation of environmental pollutants due to their nontoxicity, stability, efficiency and low cost. However, anatase  $\text{TiO}_2$  has a limitation of photo-quantum efficiency and fast recombination of photogenerated electron-hole pairs, which are expected to be improved.

Loading noble metal on the surface of  $\text{TiO}_2$  can form Schottky barrier, which acts as an electron trapper to prevent electron-hole recombination. Doping transition metal into  $\text{TiO}_2$  lattice can change the crystal structure and the band gap, i.e., changing absorption range of  $\text{TiO}_2$ . In this thesis, our research focuses on the synthesis of  $\text{TiO}_2$  with high activity in both liquid and gas phases, through a one-step low-temperature hydrothermal method in aqueous solution using tetra-n-butyl titanate and metal-salt as precursors. Anatase  $\text{TiO}_2$  loaded with crystalline Ag, doped with W and loaded/doped with Ag/W two elements were prepared. The structure and morphology were characterized by Auger electron spectroscopy (AES), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV-Vis absorption spectra (UV-Vis) and fluorescence spectra (FS). Photocatalytic activity was tested with photocatalytic degradation of hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas in gas phase and methyl blue in liquid phase. The relation between structure, morphology, amount of loaded/doped metal and photocatalytic activity was discussed and reaction mechanism of one step low-temperature hydrothermal method was proposed.

The results show that (1)  $\text{TiO}_2$  loaded with nano Ag particles prepared by our one step low-temperature method are crystalline, which is different with amorphous nano Ag prepared by the conventional UV reduction deposition method. Since crystalline nano Ag traps photogenerated electrons a lot more easily than amorphous one, the recombination of photo-electron and photo-hole is restrained, the

photocatalytic activity of Ag/TiO<sub>2</sub> is significantly improved on H<sub>2</sub>S degradation. The H<sub>2</sub>S adsorption capability is in proportion to the Ag concentrations. The Ag/TiO<sub>2</sub> sample with amount of nano Ag 4.5 wt% has the best photocatalytic activity which is 3.1 times over that of TiO<sub>2</sub>; (2) W<sup>6+</sup> of the prepared W/TiO<sub>2</sub> is found to enter the lattice by substituting for Ti<sup>4+</sup>, and form a W<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> solid solution, which is propitious to thermal stability of TiO<sub>2</sub> nanoparticles. The photocatalytic activity of W/TiO<sub>2</sub> is improved on degradation of methyl blue, and the W/TiO<sub>2</sub> with amount of W 3 wt% is the best; (3) The prepared (Ag, W)/TiO<sub>2</sub> with W<sup>6+</sup> ion substitute for Ti<sup>4+</sup> ion in lattice and Ag nanoparticles loaded on the surface of TiO<sub>2</sub>, has a band gap of 3.0eV and the light response range is expanded. The photocatalytic activity on methyl blue degradation is between that of W/TiO<sub>2</sub> and Ag/TiO<sub>2</sub>, and the best ratio of Ag and W is 1:2. The photocatalytic activity on H<sub>2</sub>S degradation is better than TiO<sub>2</sub>. (Ag, W)/TiO<sub>2</sub> is a potential candidate with good photocatalytic activity in both gas and liquid phases.

One-step low-temperature hydrothermal method has advantages that the process and reaction condition are simple, and low cost because TiO<sub>2</sub> loaded with crystalline metal nano particles can be obtained by one-step only in aqueous solution without any other reagents, and a following calcination process is not necessary. Metal ion and TiO<sub>2</sub> have excellent dispersion since precursors of Ti and Ag are uniformly mixed. The size and crystallinity of the nano metal can be easily adjusted by the amount of precursors and the hydrothermal temperature. One-step low-temperature hydrothermal method is a very promising approach to prepare metal loaded/doped TiO<sub>2</sub>.

**Key words:** TiO<sub>2</sub>; one-step low-temperature hydrothermal method; crystalline Ag-loaded; W-doped; photocatalytic activity



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